Inorg. Chem. **2007**, *46*, 7193–7198

Inorganic Chemistry
Article

Electrophilic Ruthenium(VI) Nitrido Complex Containing Kläui's Oxygen Tripodal Ligand

Xiao-Yi Yi,[†] Tony C. H. Lam,[†] Yiu-Keung Sau,[†] Qian-Feng Zhang,[‡] Ian D. Williams,[†] and Wa-Hung Leung*,[†]

Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, People's Republic of China, and Department of Applied Chemistry, Anhui University of Technology, Ma'anshan, Anhui 243002, People's Republic of China

Received April 23, 2007

Treatment of [n-Bu$_4$N][Ru(N)Cl$_4$] with [AgL$_{OEt}$] (L$_{OEt}{}^-$ $=$ [(η^5-C$_5$H$_5$)Co{P(O)(OEt)$_2$}$_3$]$^-$) afforded the ruthenium(VI) nitrido complex [L$_{OEt}$Ru(N)Cl$_2$] (**1**), which reacted with PPh$_3$ to give the ruthenium(IV) phosphiniminato complex [L$_{OEt}$Ru(NPPh$_3$)Cl$_2$] (**2**). The cyclic voltammogram of **2** displays the Ru$^{IV/III}$ couple at ca. 0 V vs ferrocenium/ferrocene. Treatment of **1** with Me$_3$NO afforded [L$_{OEt}$Ru(NO)Cl$_2$] (**3**), which reacted with Ag(OTf) (OTf$^-$ $=$ triflate) to give the chloro-bridged tetranuclear ruthenium/silver complex [L$_{OEt}$Ru(NO)Cl$_2$]$_2$[Ag(OTf)]$_2$ (**4**). Treatment of **1** with Na$_2$S$_2$O$_3$ gave the thionitrosyl complex [L$_{OEt}$Ru(NS)Cl$_2$] (**5**). The solid-state structures of **1**–**4** have been established by X-ray crystallography.

Introduction

Transition-metal nitrido complexes are of significance because of their applications in organic transformations[1] and their involvement in metal-mediated nitrogen fixation reactions.[2] Of special interest are late-transition-metal nitrido complexes that exhibit electrophilic behavior.[3] Reactions of electrophilic osmium(VI) nitrido complexes containing polypyridyl and trispyrazolyl ligands with a range of nucleophiles including phosphines, Me$_3$NO, thiols, CN$^-$, N$_3{}^-$, amines,[4] PhMgCl,[5] BPh$_3$,[6] and cyclohexadiene[7] have been studied extensively. Recently, Lau and co-workers demonstrated that ruthenium(VI) nitrido complexes are considerably more reactive than the osmium(VI) congeners. For example, ruthenium(VI) salen nitrido complexes underwent facile bimolecular N···N coupling in polar solvents[8] and reacted with alkenes in the presence of Lewis bases such as pyridine to give deprotonated aziridine complexes.[9]

While osmium(VI) nitrido compounds containing facially coordinated tripodal N- and O-donor ligands are known,[4−7,10,11] analogous ruthenium compounds have not been reported. To better understand the reactivity of electrophilic metal nitrido compounds, we sought to synthesize ruthenium(VI) nitrido compounds with Kläui's tripodal ligands [CpCo{P(O)(OR)$_2$}$_3$]$^-$ (denoted as L$_{OR}{}^-$)[12] (Chart 1).

Although L$_{OR}{}^-$ are strong π-donating ligands that can stabilize highly oxidizing metal ions, relatively few high-valent Ru−L$_{OR}$ compounds, e.g., the ruthenium(V) oxo compounds [(L$_{OR}$)Ru(O)]$_2$(μ-O)$_2$ (R $=$ Me, Et),[13] have been isolated to date. In this paper, we report on the synthesis and crystal structure of a ruthenium(VI) nitrido compound with the Kläui's tripodal ligand L$_{OEt}{}^-$ and its reactions with PPh$_3$, Me$_3$NO, and S$_2$O$_3{}^{2-}$.

---

* To whom correspondence should be addressed. E-mail: chleung@ust.hk.

[†] The Hong Kong University of Science and Technology.

[‡] Anhui University of Technology.

(1) (a) Groves, J. T.; Takahashi, T. *J. Am. Chem. Soc.* **1983**, *105*, 2073. (b) Bois, J. D.; Tomooka, C. S.; Hong, J.; Carreira, E. M. *Acc. Chem. Res.* **1997**, *30*, 364 and references cited therein. (c) Leung, S. K.-Y.; Huang, J.-S.; Liang, J.-L.; Che, C.-M.; Zhou, Z.-Y. *Angew. Chem., Int. Ed.* **2003**, *42*, 340.

(2) Weare, W. W.; Dai, X.; Byrnes, M. J.; Chin, J. M.; Schrock, R. R.; Müller, P. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 17099.

(3) Nugent, W. A.; Mayer, J. M. *Metal*−*Ligand Multiple Bonds*; John Wiley & Sons: New York, 1988.

(4) Meyer, T. J.; Huynh, M. H. V. *Inorg. Chem.* **2003**, *42*, 8140 and references cited therein.

(5) Crevier, T. J.; Bennett, B. K.; Soper, J. D.; Bowman, J. A.; Dehestani, A.; Hrovat, D. A.; Lovell, S.; Kaminsky, W.; Mayer, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 1059.

(6) Grevier, T. J.; Mayer, J. M. *Angew. Chem., Int. Ed.* **1998**, *37*, 1891.

(7) Maestri, A. G.; Cherry, K. S.; Toboni, J. J.; Brown, S. N. *J. Am. Chem. Soc.* **2001**, *123*, 7459.

(8) Man, W.-L.; Tang, T.-M.; Wong, T.-W.; Lau, T.-C.; Peng, S.-M.; Wong, W.-T. *J. Am. Chem. Soc.* **2004**, *126*, 478.

(9) Man, W.-L.; Lam, W. W. Y.; Yiu, S.-M.; Lau, T.-C.; Peng, S.-M. *J. Am. Chem. Soc.* **2004**, *126*, 15336.

(10) Koch, J. L.; Shapley, P. A. *Organometallics* **1997**, *16*, 4071.

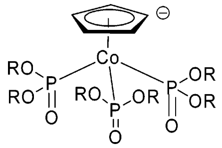
(11) Leung, W.-H.; Chan, E. Y. Y.; Lai, T. C. Y.; Wong, W.-T. *J. Chem. Soc., Dalton Trans.* **2000**, 51.

(12) Kläui, W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 627.

(13) Power, J. M.; Evertz, K.; Henling, L.; Marsh, R.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chem.* **1990**, *29*, 5058.

10.1021/ic7007683 CCC: \$37.00

Chart 1



$L_{OR}^{\ominus}$

Experimental Section

General Considerations. All manipulations were carried out under nitrogen by standard Schlenk techniques. Solvents were purified, distilled, and degassed prior to use. NMR spectra were recorded on a Bruker ARX 300 or Varian Mercury 300 spectrometer operating at 300, 75.5, 121.5, and 282.5 MHz for ^{1}H, ^{13}C, ^{31}P, and ^{19}F, respectively. Chemical shifts (δ, ppm) were reported with reference to $SiMe_4$ (^{1}H and ^{13}C), H_3PO_4 (^{31}P), and $CF_3C_6H_5$ (^{19}F). IR spectra were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer and mass spectra on a Finnigan TSQ 7000 spectrometer. Cyclic voltammetry was performed with a Princeton Applied Research (model 273A) potentiostat. The working and reference electrodes are glassy carbon and $Ag/AgNO_3$ (0.1 M in MeCN), respectively. Potentials were reported with reference to the ferrocenium/ferrocene couple. Elemental analyses were performed by Medac Ltd., Surrey, U.K. [n-Bu_4N][$Ru(N)Cl_4$][14] and [AgL_{OEt}][15] were prepared according to literature methods. $Ru(NO)Cl_3\cdot xH_2O$ was purchased from Strem Ltd. and used as received.

Preparation of [$L_{OEt}Ru(N)Cl_2$] (1). To a solution of [n-Bu_4N][$Ru(N)Cl_4$] (332 mg, 0.66 mmol) in MeCN/Et_2O (1:1, v/v; 40 mL) was added AgL_{OEt} (400 mg, 0.62 mmol) in Et_2O (60 mL) over a period of 30 min. The resulting mixture was stirred at room temperature overnight, during which the color changed from darkish brown to tan. The AgCl precipitate was filtered off, and the volatiles were removed in vacuo. The brown oily residue was washed with water (5 × 10 mL) and extracted with $CHCl_3$ (2 × 15 mL). The solvent was pumped off, and the residue was extracted with Et_2O. Evaporation of the solvent afforded a brown crystalline solid. Yield: 118 mg (26%). Recrystallization of the crude product from Et_2O at −18 °C gave reddish-brown single crystals that were suitable for X-ray diffraction. ^{1}H NMR ($CDCl_3$): δ 1.22 (t, 6H, CH_3), 1.32 (t, 6H, CH_3), 1.36 (t, 6H, CH_3), 4.01−4.11 (m, 4H, OCH_2), 4.26−4.29 (m, 8H, OCH_2), 5.08 (s, 5H, C_5H_5). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 109.8 (t, $J = 146$ Hz), 126.4 (d, $J = 146$ Hz). MS (ESI): m/z 719.9 (M^+), 686.0 ($M^+ - Cl$). Anal. Calcd for $C_{17}H_{35}Cl_2CoNO_9P_3Ru$: C, 28.31; H, 4.89; N, 1.94. Found: C, 28.59; H, 5.00; N, 1.64.

Reaction of 1 with Silver Triflate. To **1** (15 mg, 0.02 mmol) in CH_2Cl_2 (5 mL) was added Ag(OTf) (10 mg, 0.04 mmol). The reaction mixture was sonicated in an ultrasound bath at room temperature for 30 min and filtered. Evaporation of the solvent afforded an orange oil that did not crystallize. ^{1}H NMR ($CDCl_3$): δ 1.34−1.39 (m, 18H, CH_3), 4.21−4.27 (m, 12H, OCH_2), 5.16 (s, 5H, C_5H_5). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 110.4 (t, $J = 146$ Hz), 127.0 (d, $J = 146$ Hz). ^{19}F{^{1}H} NMR ($CDCl_3$): δ −77.3. MS (ESI): m/z 651.0 ($M^+ - 2Cl$).

Preparation of [$L_{OEt}Ru(NPPh_3)Cl_2$] (2). To a solution of **1** (69 mg, 0.096 mmol) in CH_2Cl_2 (5 mL) was added PPh_3 (25 mg, 0.095 mmol) in CH_2Cl_2 (10 mL) at −30 °C dropwise, and the mixture was stirred at room temperature overnight. The volatiles were removed in vacuo, and the residue was washed with hexane and extracted with Et_2O. Concentration and cooling at −18 °C afforded reddish-brown single crystals that were suitable for X-ray diffraction. Yield: 50% (47 mg). μ_{eff} ($CHCl_3$, Evans method) = 2.6 μ_B. Anal. Calcd for $C_{35}H_{50}Cl_2CoNO_9P_4Ru$: C, 42.70; H, 5.12; N, 1.42. Found: C, 42.50; H, 5.32; N, 1.39.

Preparation of [$L_{OEt}Ru(NO)Cl_2$] (3). Method A. A mixture of $Ru(NO)Cl_3\cdot xH_2O$ (156 mg, 0.66 mmol) and NaL_{OEt} (346 mg, 0.62 mmol) in tetrahydrofuran (THF; 40 mL) was refluxed overnight. The solvent was removed, and the residue was washed with hexane/Et_2O. Evaporation of the solvent afforded a brown solid. Recrystallization from CH_2Cl_2/hexane afforded brown single crystals that were suitable for X-ray diffraction. Yield: 340 mg (74%). ^{1}H NMR ($CDCl_3$): δ 1.25−1.34 (overlapping t, 18H, CH_3), 4.07−4.19 (m, 8H, OCH_2), 4.29−4.34 (m, 4H, OCH_2), 5.09 (s, 5H, C_5H_5). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 121.4 (s). IR (KBr, cm^{-1}): 1865 (s, ν_{NO}). MS (FAB): m/z 737.0 (M^+). Anal. Calcd for $C_{17}H_{35}Cl_2CoNO_{10}P_3Ru$: C, 27.69; H, 4.79; N, 1.90. Found: C, 27.67; H, 5.07; N, 1.83.

Method B. A mixture of **1** (36 mg, 0.05 mmol) and Me_3NO (7.5 mg, 0.1 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for 1 h. The volatiles were removed, and the residue was washed with hexane. Recrystallization from Et_2O afforded **3** in 75% yield.

Preparation of [{$L_{OEt}Ru(NO)Cl_2$}$_2${Ag(OTf)}$_2$] (4) ($OTf^- =$ triflate). A mixture of **3** (48 mg, 0.065 mmol) and Ag(OTf) (17.8 mg, 0.065 mmol) in MeCN (10 mL) was stirred at room temperature overnight. The solvent was removed, and the residue was washed with Et_2O. Recrystallization from CH_2Cl_2/Et_2O/hexane afforded pink-purple needles that were suitable for X-ray diffraction. Yield: 61 mg (93%). ^{1}H NMR ($CDCl_3$): δ 1.21−1.37 (overlapping t, 36H, CH_3), 4.09 (m, 16H, OCH_2), 4.35 (m, 8H, OCH_2), 5.13 (s, 10H, C_5H_5). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 124.0 (s). ^{19}F NMR ($CDCl_3$): δ −77.7 (OTf). IR (KBr, cm^{-1}): 1864 (ν_{NO}), 1266 (ν_{SO}). Anal. Calcd for $C_{17}H_{35}Cl_2CoNO_{10}P_3Ru$: C, 27.69; H, 4.79; N, 1.90. Found: C, 27.67; H, 5.07; N, 1.83.

Preparation of [$L_{OEt}Ru(NS)Cl_2$] (5). A mixture of **1** (40 mg, 0.055 mmol) and $Na_2S_2O_3\cdot 2H_2O$ (96 mg, 0.387 mmol) in MeCN (10 mL) was stirred overnight. The solvent was pumped off in vacuo, and the residue was washed with Et_2O (3 × 10 mL). Evaporation of the solvent afforded an analytically pure brown crystalline solid that was further recrystallized from THF/hexane. Yield: 29 mg (70%). ^{1}H NMR ($CDCl_3$): δ 1.24−1.37 (overlapping t, 18H, CH_3), 4.16−4.23 (m, 12H, OCH_2), 5.07 (s, 5H, C_5H_5). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 121.7 (s). IR (KBr, cm^{-1}): 1307 (ν_{NS}). MS (FAB): m/z 717.9 ($M^+ - Cl$). Anal. Calcd for $C_{17}H_{35}Cl_2CoNO_9P_3RuS$: C, 27.10; H, 4.68; N, 1.86. Found: C, 27.17; H, 4.78; N, 1.75.

X-ray Crystallography. Details of crystallographic data collection and refinement for **1**−**4** are summarized in Table 1. Preliminary examinations and intensity data collection were carried out on a Bruker SMART-APEX 1000 area detector diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.701\,73$ Å). The collected frames were processed with the software *SAINT*.[16] The data were corrected for absorption using the program *SADABS*. Structures were solved by direct methods and refined by full-matrix least squares on F^2 using the *SHELXTL* software package.[17] Unless stated otherwise, non-hydrogen atoms were refined with anisotropic displacement parameters. In the L_{OEt}^- ligand of **1**, each of the three

---

(14) Griffith, W. P.; Pawson, D. *J. Chem. Soc., Dalton Trans*. **1973**, 1315.

(15) Glaum, M.; Kläui, W.; Skelton, B. W.; White, A. H. *Aust. J. Chem*. **1997**, *50*, 1047.

(16) *Bruker SMART and SAINT+*, version 6.02a; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1998.

(17) Sheldrick, G. M. *SHELXTL-PLUS v.5.1 Software Reference Manual*; Bruker AXS Inc.: Madison, WI, 1997.

Table 1. Crystallographic Data and Structure Refinement Details for **1**−**4**

compound	**1**	**2**	**3**	**4**
formula	$C_{17}H_{35}O_9NP_3Cl_2CoRu$	$C_{35}H_{50}O_9NP_4Cl_2CoRu$	$C_{17}H_{35}O_{10}NP_3Cl_2CoRu$	$C_{36}H_{70}O_{26}N_2P_6F_6Cl_4Co_2Ag_2Ru_2S_2$
fw	721.27	983.54	737.27	1988.42
T, K	100(2)	100(2)	100(2)	100(2)
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a, Å	12.300(1)	9.742(1)	9.1180(7)	9.5821(6)
b, Å	18.343(2)	10.516(1)	18.177(1)	36.808(2)
c, Å	12.377(1)	21.845(3)	17.694(1)	19.022(1)
α, deg	90	82.109(3)	90	90
β, deg	96.214(2)	79.394(2)	91.041(2)	91.143(1)
γ, deg	90	70.706(2)	90	90
V, Å^3	2776.2(5)	2069.0(5)	2932.1(4)	6707.7(7)
Z	4	2	4	4
ρ_{calc}, g cm^{-3}	1.726	1.579	1.67	1.969
μ, mm^{-1}	1.551	1.101	1.473	1.95
F(000)	1464	1008	1496	3952
no. of reflns	14 574	11 651	14 621	33 644
no. of indep reflns	4574	7025	5121	11 707
R_{int}	0.0572	0.0446	0.0416	0.0825
R1, wR2 [$I > 2.0\sigma(I)$]	0.0561, 0.1260	0.0414, 0.0791	0.0307, 0.0580	0.0429, 0.0604
R1, wR2 (all data)	0.1036, 0.1424	0.0715, 0.0866	0.0453, 0.0610	0.0948, 0.0676
GOF[a]	0.933	0.984	0.955	0.975

[a] GOF = $[\sum w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[L_{OEt}Ru(NX)Cl_2]$

	X = nothing (**1**)[a]	X = PPh_3 (**2**)	X = O (**3**)
Ru−N	1.573(6)	2.032(3)	1.729(3)
Ru−O(trans to N)	2.12(2) O(8A) 2.278(8) O(8B)	2.075(3)	2.005(2)
Ru−O(cis to N)	2.030(5) 2.031(5)	2.074(3) 2.099(3)	2.063(2) 2.061(2)
Ru−Cl(1)	2.236(4) Cl(1A) 2.476(6) Cl(1B)	2.336(1)	2.332(1)
Ru−Cl(2)	2.464(8) Cl(2A) 2.21(1) Cl(2B) 2.27(1) Cl(2C)	2.352(1)	2.329(1)
N−X		1.605(3)	1.127(3)
O−Ru−O′	73.1(3)-92.3(2)	87.8(1) 87.5(1) 90.3(1)	89.92(8) 88.93(8) 86.40(8)
N−Ru−O(cis to N)	94.8(3) 94.8(3)	92.0(1) 87.0(1)	90.1(1) 95.4(1)
N−Ru−Cl		89.5(1) 96.2(1)	93.54(9) 91.36(9)
Cl−Ru−Cl′		95.15(4)	92.27(3)
Ru−N−X		135.4(2)	177.6(3)

[a] In **1**, O(8), Cl(1), and Cl(2) are 50:50, 55:45, and 42:35:23 disorder, respectively.

phosphorus atoms P(1)−P(3) was found to be 70:30 disorder and O(8) 50:50 disorder. Some ethoxy groups, Cl(1) and Cl(2), were also found to be disordered. The occupancies for the two sites of Cl(1) are 0.55 and 0.45, whereas those of Cl(2) are 0.42, 0.35, and 0.23. In **2**, the disordered ethoxy carbon C(12) was refined with occupancies of 0.5 and 0.5. Selected bond lengths and angles for **1**−**3** and **4** are listed in Tables 2 and 3, respectively.

Results and Discussion

Ruthenium(VI) Nitrido Compound. The synthesis and reactivity of Ru−L_{OEt} complexes are summarized in Scheme 1. Treatment of [n-Bu_4N][Ru(N)Cl_4] with [AgL_{OEt}] in MeCN/Et_2O afforded an oily material, which upon recrystallization afforded **1**, isolated as an air-stable orange solid. The Ru−N stretching mode was not assigned because of the overlap with the intense P═O band in the 900−1100 cm^{-1} region in the IR spectrum. Unlike the Ru(salen) analogues,[8] **1** does not undergo a bimolecular N···N coupling reaction in polar solvents such as MeOH and MeCN. Treatment of **1** with 2 equiv of Ag(OTf) (OTf^- = triflate) in CH_2Cl_2 led to the formation of AgCl along with an orange oily material that exhibits a signal at m/z 651 assignable to $[L_{OEt}Ru(N)]^+$ in the ESI mass spectrum. The ^{19}F NMR spectrum displays a singlet at δ −77.3 ppm due to the triflate ligands. Therefore, this orange species is tentatively formulated as the triflato compound "$[L_{OEt}Ru(N)(OTf)_2]$". Unfortunately, we have not been able to obtain a crystalline sample of this compound for further study.

Ruthenium(IV) Phosphiniminato Compound. As one might expect, **1** exhibits electrophilic behavior and reacts with nucleophiles such as amines and phosphines readily. The reaction of **1** with morpholine in CH_2Cl_2 resulted in an immediate change of color from brown to red. Recrystallization from CH_2Cl_2/hexane afforded an air-sensitive, paramagnetic red oil. We have not been able to crystallize this oily material, which possibly contains a ruthenium hydrazido(1−) species. Treatment of **1** with PPh_3 afforded the ruthenium(IV) phosphiniminato compound **2**, isolated as air-stable brown crystals. Compound **2** is paramagnetic with a measured μ_{eff} of ca. 2.6 μ_B, which is close to the spin-only value for two unpaired electrons. Similar magnetic moments have been found for reported ruthenium(IV) phosphiniminato compounds.[18] The cyclic voltammogram of **2** shows a reversible couple at ca. 0 V vs $Cp_2Fe^{+/0}$, which is tentatively assigned as the $Ru^{IV/III}$ couple. By comparison, the $Os^{IV/III}$ couple for the osmium analogue $[L_{OEt}Os(NPPh_3)Cl_2]$ was observed at −0.718 V vs $Cp_2Fe^{+/0}$.[11]

Ruthenium Nitrosyl and Thionitrosyl Compounds. **1** reacted readily with Me_3NO to give the nitrosyl compound **3**. The IR spectrum of **3** shows the ν_{NO} peak at ca. 1865 cm^{-1}, which is typical for ruthenium(II) nitrosyl com-

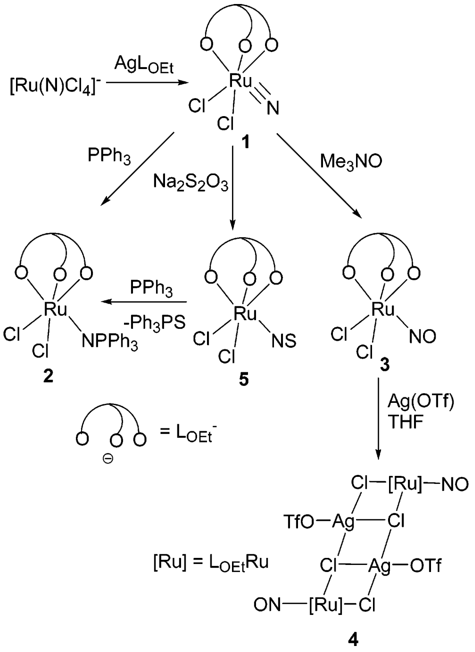
---

[18] Pawson, D.; Griffith, W. P. *J. Chem. Soc., Dalton Trans.* **1975**, 417.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **4**

Ru(1)−N(1)	1.720(5)	Ru(2)−N(2)	1.720(5)
Ru(1)−O(17)	2.006(3)	Ru(2)−O(27)	2.002(3)
Ru(1)−O(18)	2.048(3)	Ru(2)−O(28)	2.034(3)
Ru(1)−O(19)	2.040(3)	Ru(2)−C(29)	2.034(3)
Ru(1)−Cl(1)	2.350(2)	Ru(2)−Cl(2)	2.341(2)
Ru(1)−Cl(3)	2.359(2)	Ru(2)−Cl(4)	2.374(2)
N(1)−O(1)	1.149(5)	N(2)−O(2)	1.155(5)
Ag(1)−O(6)	2.280(4)	Ag(2)−O(3)	2.208(4)
Ag(1)−μ_2-Cl(3)	2.578(2)	Ag(2)−μ_2-Cl(4)	2.531(2)
Ag(1)−μ_3-Cl(1)	2.661(2)	Ag(2)−μ_3-Cl(1)	2.766(2)
Ag(1)−μ_3-Cl(2)	2.657(1)	Ag(2)−μ_3-Cl(2)	2.816(2)
O−Ru−O′	88.8(1)−91.6(1)	Cl−Ru−Cl′	90.57(5), 90.87(6)
N−Ru−Cl	91.4(2)−95.4(2)	Ru−μ_2-Cl−Ag	95.99(5), 90.35(5)
Ru−μ_3-Cl−Ag	119.11(6), 113.51(5)	Ag−μ_3-Cl−Ag′	86.12(4), 85.19(4)
O−Ag−Cl	100.7(1)−161.6(1)	Cl−Ag−Cl′	77.66(5)−116.85(5)
Ru−N−O	175.5(4), 176.6(5)		

Scheme 1



pounds.[19] Alternatively, **3** was prepared in high yield by the reaction of Ru(NO)Cl$_3$·xH$_2$O with NaL$_{OEt}$. Compound **3** exhibits a single ^{31}P NMR resonance at δ 121.4 ppm despite having two inequivalent types of phosphorus nuclei. This is in contrast with **1**, which exhibits a doublet and a triplet in the ^{31}P{^{1}H} NMR spectrum, as expected for an AB$_2$ spin system. The observation of the accidental degeneracy of the ^{31}P NMR resonance for **3** suggests that the three phosphorus nuclei have very similar chemical environments. A similar result was found for the related thionitrosyl compound **5** (vide infra).

An attempt has been made to abstract the chloride in **3** with silver(I) salts. However, instead of chloride abstraction, treatment of **3** with Ag(OTf) in CH$_2$Cl$_2$ led to isolation of a tetranuclear ruthenium/silver bimetallic compound, **4**, which has been characterized by X-ray diffraction. The IR N−O stretching frequency of **4** is almost identical with that of **3**, indicating that the Ag(OTf) moiety has little influence on the electron density of the ruthenium center. The ^{1}H and ^{31}P{^{1}H} NMR spectra of **4** in a CDCl$_3$ solution are different from those of **3**, indicating that the tetranuclear structure of **4** remained intact in solution.

The reaction between **1** and elemental sulfur led to an intractable material that did not crystallize. The thionitrosyl compound **5** was isolated in good yield by the treatment of **1** with Na$_2$S$_2$O$_3$. It may be noted that [TpOs(NS)Cl$_2$] [Tp$^-$ = hydridotris(pyrazolyl)borate] has been prepared by the reaction of [TpOs(N)Cl$_2$] with CS$_2$ + N$_3^-$,[20] propylene sulfide, S$_8$,[21] or Na$_2$S$_2$O$_3$[22] previously. The IR spectrum of **5** is almost identical with that of **3** except that the NO band was absent and that a new peak at 1307 cm^{-1} attributable to ν_{NS} appeared. The N−S stretching frequency for **5** is typical for thionitrosyl compounds.[23] The ^{31}P{^{1}H} NMR spectrum of **5** displays a singlet at δ 121.7 ppm, which is similar to that of **3**. Compound **5** has been characterized by an X-ray diffraction study.[24] Unfortunately, the structure has not been refined satisfactorily because of the severely disordered NS group. The mass spectrum of **5** shows the molecular peak at m/z 717.9 corresponding to M$^+$ − Cl. **5** is air-stable in both the solid state and solutions. The treatment of **5** with PPh$_3$ led to the formation of **2**, presumably via the nitrido compound **1**, and Ph$_3$PS. By contrast, no reaction was found between **3** and PPh$_3$.

Crystal Structures. The solid-state structures of **1**−**4** are shown in Figures 1−4, respectively. Selected bond lengths and angles for **1**−**3** and **4** are compiled in Tables 2 and 3, respectively. In each of the compounds, the ruthenium has pseudooctahedral coordination geometry with a facially coordinated L$_{OEt}^-$ ligand. Compounds **1** and **2** are isostructural with the previously reported osmium analogues [L$_{OEt}$-

---

[19] Richter-Addo, G. B.; Legzdins, P. *Metal Nitrosyls*; Oxford University Press: New York, 1992.

[20] El-Samanody, E. S.; Demadis, K. D.; Gallagher, L. A.; Meyer, T. J.; White, P. S. *Inorg. Chem.* **1999**, *38*, 3329.

[21] Crevier, T. J.; Lovell, S.; Mayer, J. M.; Rheingold, A. L.; Guzei, I. A. *J. Am. Chem. Soc.* **1998**, *120*, 6607.

[22] Wu, A.; Dehestani, A.; Saganic, E.; Crevier, T. J.; Kaminsky, W.; Cohen, D. E.; Mayer, J. M. *Inorg. Chim. Acta* **2006**, *359*, 2842.

[23] Pandey, K. K. *Prog. Inorg. Chem.* **1992**, *40*, 45.

[24] Crystal data for **5**: C$_{17}$H$_{35}$Cl$_2$CoNO$_9$P$_3$RuS, a = 9.8499(8) Å, b = 12.7196(10) Å, c = 12.5180(10) Å, β = 107.407(2)°, V = 1496.5(2) Å^3, monoclinic, Pc space group, Z = 2, ρ_{calcd} = 1.672 g cm^{-3}, T = 298(2) K, μ = 1.510 mm^{-1}, no. of data = 4182, R1 [$I > 2\sigma(I)$] = 0.0458, wR2 [$I > 2\sigma(I)$] = 0.0648, and R1 (all data) = 0.1465, wR2 (all data) = 0.0800. The N−S moiety was constrained with the Ru−N and N−S bond lengths of 1.608(8) and 1.405(8) Å, respectively, and the Ru−N−S bond angle of 169.2(11)°. No residual electron density > 1 e$^-$ Å^{-3} was observed upon convergence.

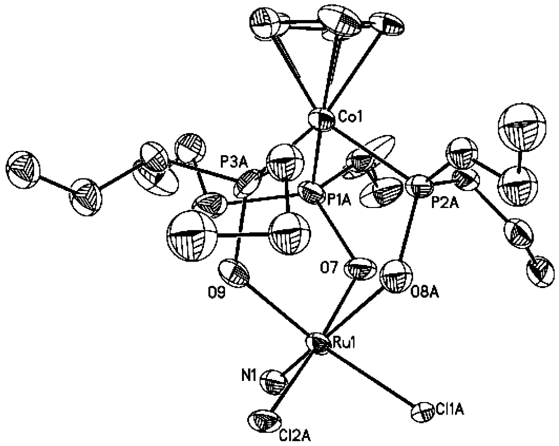


Figure 1. Molecular structure of **1**. Only positions of the disordered atoms O(8A), Cl(1A), and Cl(2A) are shown. The ellipsoids are drawn at a 30% probability level.

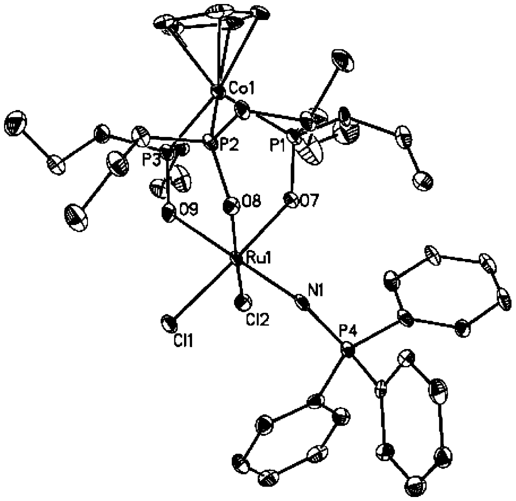


Figure 2. Molecular structure of **2**. The ellipsoids are drawn at a 30% probability level.

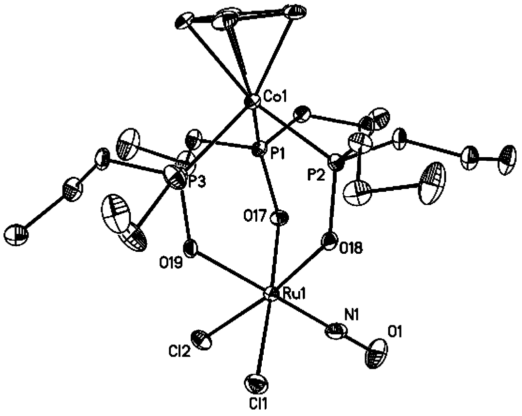


Figure 3. Molecular structure of **3**. The ellipsoids are drawn at a 30% probability level.

Os(N)Cl$_2$] and [L$_{OEt}$Os(NPPh$_3$)Cl$_2$], respectively. In **1**, the Ru−N bond length of 1.573(6) Å is short and consistent with a Ru−N triple bond. The Ru−O(8) bond [2.12(1) and 2.278(8) Å for O(8A) and O(8B), respectively] opposite to the trans-directing nitrido group was found to be longer than the other two Ru−O bonds [2.030(5) and 2.031(5) Å]. Upon the addition of PPh$_3$ and the formation of the Ru−NPPh$_3$ compound **2**, the Ru−O(trans to N) distance is shortened to 2.075(3) Å, which is similar to the Ru−O(cis to N) distances, indicative of the absence of the trans influence of the phosphiniminato group. The Ru−N distance in **2** of 2.032(3) Å is longer than that in [Ru(NPEt$_2$Ph)Cl$_3$(PEt$_2$Ph)$_2$] [1.855(5) Å][25] and consistent with a Ru−N single bond. Similar to [L$_{OEt}$Os(NPPh$_3$)Cl$_2$],[11] the Ru−N−P unit in **2** is bent with the Ru−N−P angle of 135.4(2)°. The N═P distance of 1.605(3) Å is typical for the P═N double bond.

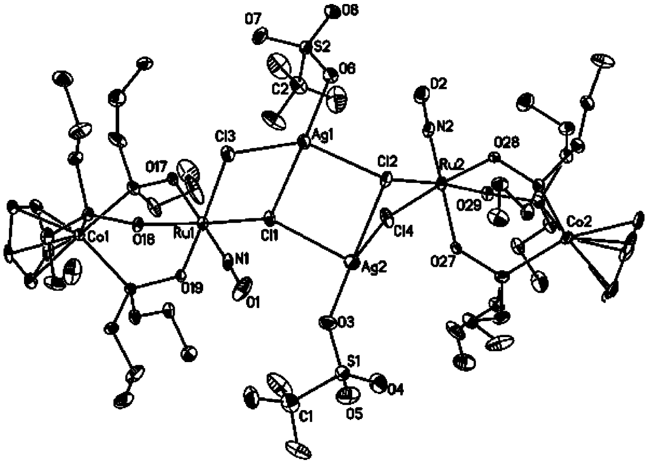


Figure 4. Molecular structure of **4**. The ellipsoids are drawn at a 30% probability level.

The Ru−N distance in **3** [1.729(3) Å] is shorter than that in **2**, suggestive of some Ru−N multiple bond character. The Ru−O(trans to NO) distance is slightly shorter than the Ru−O(cis to NO) distances, indicating the π donation from the trans P═O group to ruthenium that facilitates the Ru-to-NO back-bonding. The Ru−Cl distances in **3** [2.332(1) and 2.329(1) Å] are similar to those in **2** [2.336(1) and 2.352(1) Å]. The structure of **4** can be viewed as consisting of two {L$_{OEt}$Ru(NO)(μ-Cl)$_2$Ag(OTf)} moieties that are linked together, resulting in a Ag$_2$Cl$_2$ core. Each silver atom is four-coordinated with one terminal triflate, one μ_2-chloride, and two μ_3-chloride ligands. The average Ag−O, Ag−μ_2-Cl, and Ag−μ_3-Cl distances are 2.244, 2.558, and 2.725 Å, respectively. The Ru−Cl, Ru−N, and Ru−O distances in **4** are similar to those in **3**. It may be noted that the Ru−O(cis to O) distances in the ruthenium(II) nitrosyl compounds **3** and **4** are not significantly different from that in the ruthenium(VI) nitrido compound **1**. The similarity in M−L(cis to N) distances between metal nitrido and nitrosyl compounds is well documented and has been found for other systems such as [Mn(N)(CN)$_5$]$^{3-}$/[Mn(NO)(CN)$_5$]$^{3-}$ and [Re(N)(CN)$_4$(H$_2$O)]$^{2-}$/[Re(NO)(CN)$_4$(H$_2$O)]$^{3-}$.[26] A recent theoretical study showed that the inner electronic structures of [Mn(N)(CN)$_5$]$^{3-}$ and [Mn(NO)(CN)$_5$]$^{3-}$ are almost the same and that [Mn(NO)(CN)$_5$]$^{3-}$ behaves more closely to Mn^{V} than to

---

(25) Phillips, F. L.; Skapski, A. C. *J. Chem. Soc., Chem. Commun.* **1974**, 49.

(26) Bendix, J.; Deeth, R. J.; Weyhermüller, T.; Bill, E.; Wieghardt, K. *Inorg. Chem.* **2000**, *39*, 930.

Mn^{I}.[27] Therefore, the ruthenium formal oxidation states in **1**, **3**, and **4** are assigned for electron-bookkeeping purposes only and do not reflect the real charges on ruthenium.

Concluding Remarks

In summary, we have synthesized and structurally characterized a ruthenium(VI) nitrido compound containing the oxygen tripodal ligand L_{OEt}^-, which unlike the salen analogues is stable with respect to a bimolecular N•••N coupling reaction. This ruthenium(VI) nitrido compound was found to be electrophilic and reacted with PPh_3, Me_3NO, and $S_2O_3^{2-}$ to give phosphiniminato, nitrosyl, and thionitrosyl compounds, respectively. The treatment of **3** with Ag(OTf) afforded a chloro-bridged ruthenium/silver bimetallic compound. The isolation of compounds of the formula $[L_{OEt}Ru(X)Cl_2]$, where X is a heteroatom group, may offer an opportunity to investigate the effect of Ru−X π bonds on the reactivity and electronic structure of such compounds.

Acknowledgment. We thank Dr. Herman H. Y. Sung for solving the crystal structures. Financial support from the Hong Kong Research Grants Council (Project Nos. 602203 and DAG05/06.SC18) is gratefully acknowledged. Q.-F.Z. thanks the Science and Technological Fund of Anhui Province, People’s Republic of China, for the Outstanding Youth Award (Grant 06046100).

Supporting Information Available: Tables of crystal data, final atomic coordinates, anisotropic thermal parameters, and complete bond lengths and angles for complexes **1**−**4** (in CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

IC7007683

---

(27) Hummel, P.; Gray, H. B. *Coord. Chem. Rev.* **2007**, *251*, 554.